STATE OF ILLINOIS
ENVIRONMENTAL PROTECTION AGENCY

INTER-OFFICE CORRESPONDENCE

DATE: June 7, 1974

MEMO TO: Gary Melvin, Episode Supervisor

FROM: Charles B. Salowitz, Region II

SUBJECT: The Sherwin Williams Co. - Incident of May 31, 1974
11541 South Champlain Avenue
Chicago, Illinois 60628
Geo Code: 031 600 AHO

Incident Contact: William A. Starkovich
Title: Director of Safety
Telephone: 264-8800 ext. 2581

Incident follow-up inspection date: June 3, 1974; 9:30-11:30 A.M.

Weather: June 3; Temp: 76°F, Wind: Southwest, 11 M.P.H.
Humidity: 54%, Sky: Sunny

The author and Mr. Clifford Click, Permit Section, met with Mr. Kenneth R. Brown, General Manager. Mr. Brown stated that the SO_3 spill resulted from a valve which was not properly closed. Approximately 100 gallons was emitted before a man with an acid suit was able to close the valve. Mr. Brown referred the author to Mr. William A. Starkovich, Director of Safety.

Mr. Starkovich explained that he first received a telephone call from the plant notifying him of a spill at 2:55 p.m. on Friday, May 31, 1974- The material involved was Sulfan (Sulfur Trioxide in liquid form, SO_3), which reacts with ambient humidity to form H_2SO_4 acid mist.

Mr. Starkovich related the following scenario. On the morning of May 31, 1974, repair work had been performed on a pump in the SO_3 system (see attached sketch). The system is entirely enclosed in a building and consists of a 14,000 gallon tank, a pump to the "day" tank, a 1,000 gallon "day" tank, a plug-type shut-off valve, a 1/2" bleeder valve with nozzle, a pump to the reactor vessel, and the reactor vessel. The pump had been returned to the system. A workman then opened the shut-off valve just below the "day" tank. He proceeded to the bleeder valve to bleed the air from the pipe. The material is gravity fed from the "day" tank to the pump. As the worker bled the air from the line, a stream of SO_3 shot out at him. The worker's startled reaction was to attempt to close the

plug-type shut-off valve, above the bleeder valve. In his excitement he stripped a set screw in the shut-off valve linkage system. When Mr. Starkovich arrived at the site, the shut-off valve linkage system was in the closed position but the valve was actually still open. Believing the valve to be closed, the decision was made to wait about 5 minutes until the material in the pipe below the shut-off valve could drain out and react. After 10 minutes, Mr. Starkovich realized that the shut-off valve must still have been open. The first attempt to get to the shut-off valve was thwarted by the acid mist in the building. The second attempt, by a different route, was successful. The shut-off valve was closed with a wrench. Within a few minutes the emissions had subsided and only a small patch of ground near the building was still fuming. The incident encompassed approximately 45 minutes from start to end.

Mr. Starkovich explained that the workman had followed the standard operating procedure in bleeding air from the SO_3 line. The emission of a slight amount of SO_3 from the bleeder valve is the normal indication that the line is properly bled.

Mr. Starkovich explained that acid masks were available in the area of the plant where the spill occurred. The workman passed the safety masks as he went from the bleeder valve to the shut-off valve mechanism immediately outside of the building.

During the spilling of material, an acid cloud extended approximately 6 feet out of the door on the north side of the building. The entire room was filled with an acid mist cloud, with the major emissions to the atmosphere being from an open hatch in the roof of the room. The plume from the hatch extended southwest and reached ground level an estimated 100 feet from the emission point, on the plant property. Mr. Starkovich stated that there was no discernible odor of sulfuric acid mist at a distance of 200 feet from the emission source. He estimated the amount of material lost to be 2000 lbs. (139 gallons at 14.4 lbs/gal.

Mr. Starkovich explained that he had called the Chicago Fire Department and Chicago Department of Environmental Control. The Police Department responded independently. One Fire Department "Flying Squad" was dispatched to the site with acid suits and respirators.

Actions taken subsequent to the spill included spreading "oil-dry" (an inert clay used for absorbing oil spills) on the ground near the door, and on the floor within the plant. The saturated oil-dry was then removed to a remote area on the plant property. The oil-dry was covered with soda ash and soaked with water to convert any remaining

SO_3 to H_2SO_4 and then neutralize the acid. On Saturday, June 1, 1974, the oil-dry was turned over and neutralized again, until there were no emissions from it.

Mr. Starkovich stated that a back-up plan had been developed in the event that the leak could not be stopped. A truck of dry ice had been ordered to pack the leak and the pipe. This action would suppress the temperature below the 16.9°C (62.4°F) required to solidify the material in the pipe. With the solidified material plugging the pipe, the plume would dissipate and definitive action could be based on a re-analysis of the situation.

Mr. Starkovich explained that audio gauges are used to test the tank integrity. Such testing had been performed on an irregular basis until May, 1974. Recently, a schedule of regular inspections of all tanks containing hazardous materials was initiated (this action was inspired by the Bulk Terminals Incident of April 26 through May 10, 1974). Inspections are planned for each tank, once every six months, for the near future. Mr. Starkovich expects to reduce this schedule to annual inspections for tanks which show no changes.

Shortly after the Bulk Terminals Incident, Mr. Starkovich met with Mr. Brown and other management personnel to establish incident action plans. One result of that meeting was to contact Allied Chemical Company (Sherwin-Williams' supplier of SO_3), to determine appropriate action for control of an SO_3 spill. Unfortunately, Allied's test programs had not resulted in a viable control method. The foams which were tested to cover the spill, and isolate the SO_3 from ambient moisture, had sufficiently high moisture content that the foam reacted with the SO_3. Mr. Starkovich stated that he has ordered a foam with a very low moisture content to use in case of further SO_3 spills. Another result of the meeting was that Mr. Starkovich has ordered additional acid suits (Sherwin-Williams already has three types of acid suits), manufactured under the model name of "Acid Master". These suits use self-contained air packs and were found to be far superior to other suits during the Bulk Terminals incident. However, these suits are hand-made on special order only, and there is presently a nine-month back order time. In addition to these suits, an emergency acid cart is being assembled which can be transported to any area of the plant.

Mr. Starkovich stated that there are plans to dike the 14,000 gallon SO_3 tank, with the dike being within the building. This would provide the ability to seal the building in case of a spill.

Recommendations

1. No further action be taken regarding the SO_3 incident.

2. In view of Sherwin-Williams' long history of hazardous chemical storage without major incident, their participation in the formulation of hazardous chemical regulations (storage, handling, and transport) should be solicited by the Standards Section. Their knowledge of adequate and practical safety precautions should prove invaluable in drafting such regulations.

CBS:bjw

cc: Miles A. Zamco, Surveillance Manager
Jack Coblenz, Technical Services
Gary Patzlaff, Standards Section
Marshall Monarch, Standards Section
Karl Franson, Region
Region II Files

Derivation: Absorption of sulfur dioxide in water.
Grades: Technical; C.P.
Containers: Carboys; drums.
Hazard: Highly toxic by ingestion and inhalation; strong irritant to tissue.
Uses: Organic synthesis; bleaching straw and textiles, etc.; paper manufacture; wine manufacture; brewing; metallurgy; ore flotation; medicine; reagent in analytical chemistry; sulfites; as preservative for fruits, nuts, foods, wines; disinfecting ships; refining crude oils and paraffins.
Shipping regulations: (IATA) Other restricted articles; no label required. (ICC, CG) White label.

sulfurous oxychloride. See thionyl chloride.

sulfur oxychloride. See thionyl chloride.

sulfur subchloride. See sulfur chloride.

sulfur tetrafluoride SF_4.
Properties: A gas; m.p. −124°C; b.p. −40°C; decomposes in water. Noncombustible.
Grade: Available in cylinders at 90-94% purity.
Hazard: Highly toxic by inhalation; strong irritant to eyes and mucous membranes. Tolerance (as F), 2.5 mg. per cubic meter of air.
Uses: Fluorinating agent for making water and oil repellents, and lubricity improvers.
Shipping regulations: (IATA) Nonflammable gas. Green label. Not acceptable on passenger planes. (ICC, CG) Poison gas label.

sulfur trioxide (sulfuric anhydride) SO_3; $(SO_3)_n$
Properties: Exists in three solid modifications; alpha, m.p. 62°C; beta, m.p. 32.5°C; gamma, m.p. 16.8°C. The alpha form appears to be the stable form but the solid transitions are commonly slow; a given sample may be a mixture of the various forms, and its m.p. not constant. The solids sublime easily. All three forms boil at 45°C.
Hazard: Highly toxic; strong irritant to tissue. Oxidizing agent. Fire risk in contact with organic materials. Stabilized form requires MCA warning label. An explosive increase in vapor pressure occurs when the alpha form melts. The anhydride combines with water, forming sulfuric acid and evolving a large amount of heat.
Containers: (Stabilized, liquid) 750-lb drums; tank cars.
Uses: Sulfonation of organic compounds, especially nonionic detergents. Usually generated in plant where it is to be used.
Shipping regulations: (Stabilized) (ICC, CG) Corrosive liquid. White label. (IATA) (Beta or gamma, stabilized) Corrosive liquid. White label. (Beta or gamma, not stabilized, and alpha with or without stabilizer) Not acceptable.

sulfuryl chloride (chlorosulfuric acid; sulfonyl chloride; sulfuric chloride; sulfuric oxychloride) SO_2Cl_2.
Properties: Colorless liquid. Pungent odor. Rapidly decomposed by alkalies and by hot water. Soluble in glacial acetic acid. Sp. gr. 1.667 at 20°C; b.p. 69.2°C; m.p. −54°C; vapor density 4.6.
Derivation: (a) By heating chlorosulfonic acid in the presence of catalysts. (b) From sulfur dioxide and chlorine in the presence of either activated carbon or camphor.
Grades: Technical.
Containers: 5-gal carboys; 55-gal drums; 725-lb drums.
Hazard: Highly toxic; strong irritant to tissue. MCA warning label.
Uses: Organic synthesis (chlorinating agent, dehydrating agent; acylating agent); pharmaceuticals; dyestuffs; rubber-base plastics; rayon; poison gases; solvent; catalyst.
Shipping regulations: (ICC, CG, IATA) Corrosive liquid. White label.

sulfuryl fluoride SO_2F_2.
Properties: Colorless gas; m.p. −136.7°C; b.p. −55.4°C. Slightly soluble in cold water and most organic solvents. Noncombustible.
Containers: Steel cylinders.
Hazard: Highly toxic by inhalation. Tolerance 5 ppm in air.
Uses: Insecticide; fumigant.
Shipping regulations: (ICC, CG, IATA) Nonflammable gas. Green label.

"Sulmet."[57] Trademark for sulfamethazine.

"Sulphon."[307] Trademark for acid dyestuffs used on wool and silk; fair to good fastness to light, good fastness to washing, etc. Can be used on leather and paper.

"Sulphonated Olevene."[309] Trademark for a sulfonated synthetic olive oil; used for finishing textiles as a softener and plasticizer.

sultam acid. See *1,8-naphthosultam-2,4-disulfonic* acid.

"Sul-Thi-Zol."[123] Trademark for veterinary sodium sulfathiazole.

summer savory oil. See savory oil.

"Sumstar" 190.[212] Trademark for a polymeric dialdehyde. A fine, nonvolatile, virtually odorless powder. Produced by highly specific periodate oxidation of the anhydroglucose units of starch. Bulk density 40 to 42 lbs/cu ft.
Uses: Film-forming agents, adhesives, leather, and resins.

"Sunaptic."[494] Trademark for three grades of naphthenic acids having an average molecular weight of 310, 340, and 415.
Uses: Plasticizers; corrosion and rust inhibitors; cleaning, defoaming, foaming, dispersing, emulsifying and wetting agents; metallic naphthenates.

"Sun Colors."[134] Trademark for a series of lightfast pigments resistant to heat and chemicals based on heavy metal modification of titanium dioxide.

"Sundex" Oils.[494] Trademark for a series of aromatic process and extender oils. Recommended for rubber processing where color is not a problem.
Uses: Plasticizers, softeners, and aid processing and breakdown.

sunflower cake. The presscake resulting from hydraulic pressure expression of sunflower seeds. Typical analysis: proteins 21.0%; fats 8.5%; fiber 48.9%; water 10.2%; ash 11.4%.
Containers: Bags; bulk.
Uses: Cattle food; fertilizer ingredient.

sunflower meal. The mealy form assumed by sunflower seeds after crushing and heating. If the oil cake is ground the product again is in this mealy form. It contains 55-60% protein.
Uses: Animal feed; fertilizers.

sunflower oil.
Properties: Pale yellow semidrying oil; mild taste; pleasant odor. Soluble in alcohol, ether, chloroform and carbon disulfide. Sp. gr. 0.924-0.926; iodine value 130-135; refractive index 1.4611. Nontoxic. Combustible.

SHERWIN WILLIAMS Co
CHICAGO ILL

C. B. Salowitz
6-7-74

SO_3 STORAGE

ROUGH SKETCH - NOT TO SCALE